Supporting Information:

Catalytic Mechanisms of Oxygen-Containing Groups over Vanadium Active Sites in an Al-MCM-41 Framework for Production of 2,5-Diformylfuran from 5-Hydroxymethylfurfural

Li-Juan Liu[a], Zhao-Meng Wang[a], Ya-Jing Lyu[b], Jin-Feng Zhang[a], Zhou Huang[a], Ting Qi[a], Zhen-Bing Si[a], Hua-Qing Yang[a*], Chang-Wei Hu[b]

[a] *College of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, P.R. China*
[b] *Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, P.R. China*

*Correspondence to:
H.-Q. Yang; e-mail: huaqingyang@scu.edu.cn; Fax: 86 28 85415608; Telephone: 86 28 85415608

Catalysis Science & Technology

content

The equations for calculating TOF according to the energetic span model:

Based on transition state theory (TST), the TOF can be evaluated by eqn (i) and (ii), in which δE (the energetic span) is defined as the energy difference between the summit and trough of the catalytic cycle.

$$\mathrm{TOF} = \frac{k_B T}{h} e^{-\frac{\delta E}{RT}} \qquad \text{(i)}$$

$$\delta E = \begin{pmatrix} G_{\mathrm{TDTS}} - G_{\mathrm{TDI}} & \text{if TDTS appears after TDI} \\ G_{\mathrm{TDTS}} - G_{\mathrm{TDI}} + \Delta G_r & \text{if TDTS appears before TDI} \end{pmatrix} \qquad \text{(ii)}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and h is the Planck constant. G_{TDTS} and G_{TDI} are the Gibbs free energies of the TOF determining transition state (TDTS) and the TOF determining intermediate (TDI), and ΔG_r is the global free energy of the whole cycle.

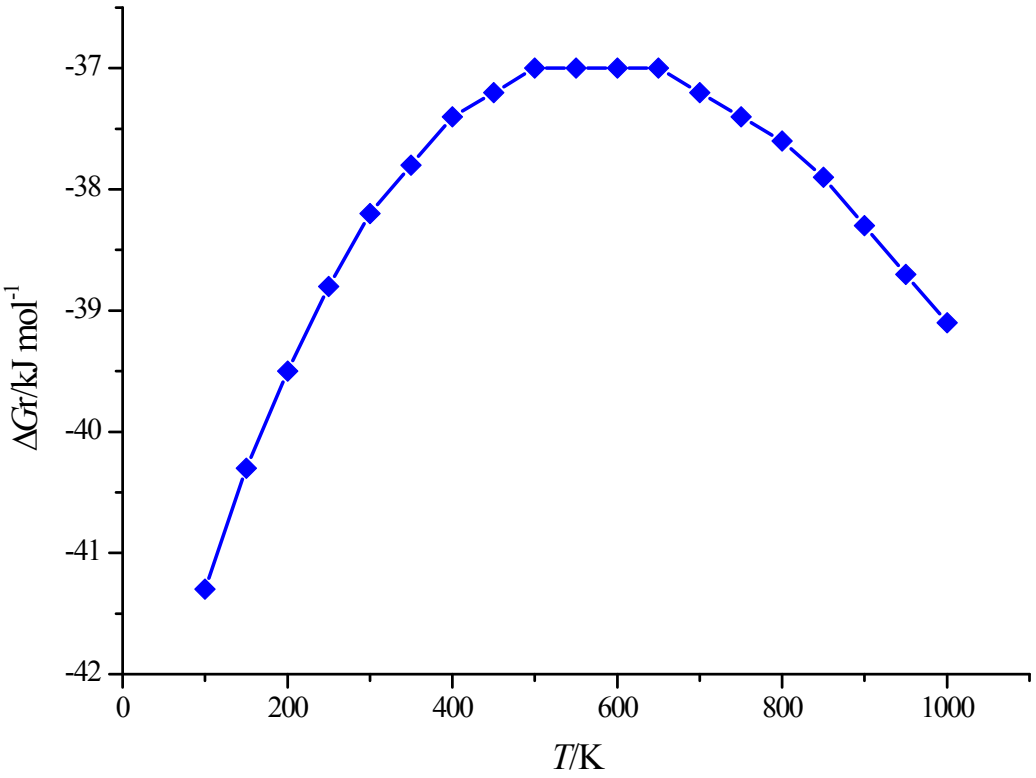
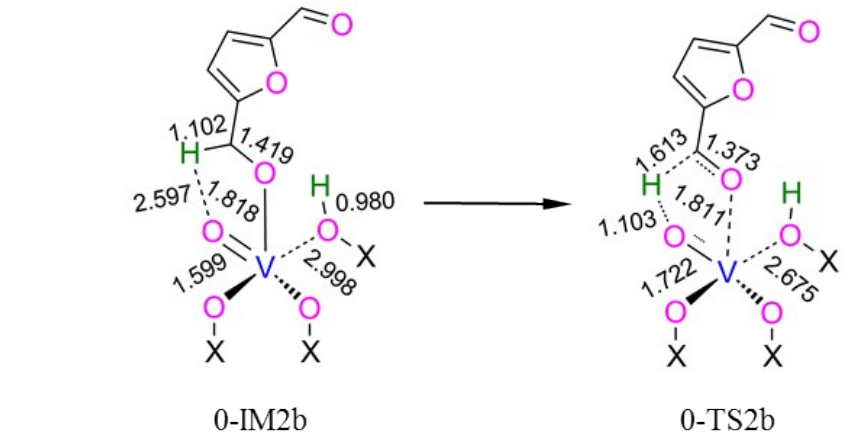
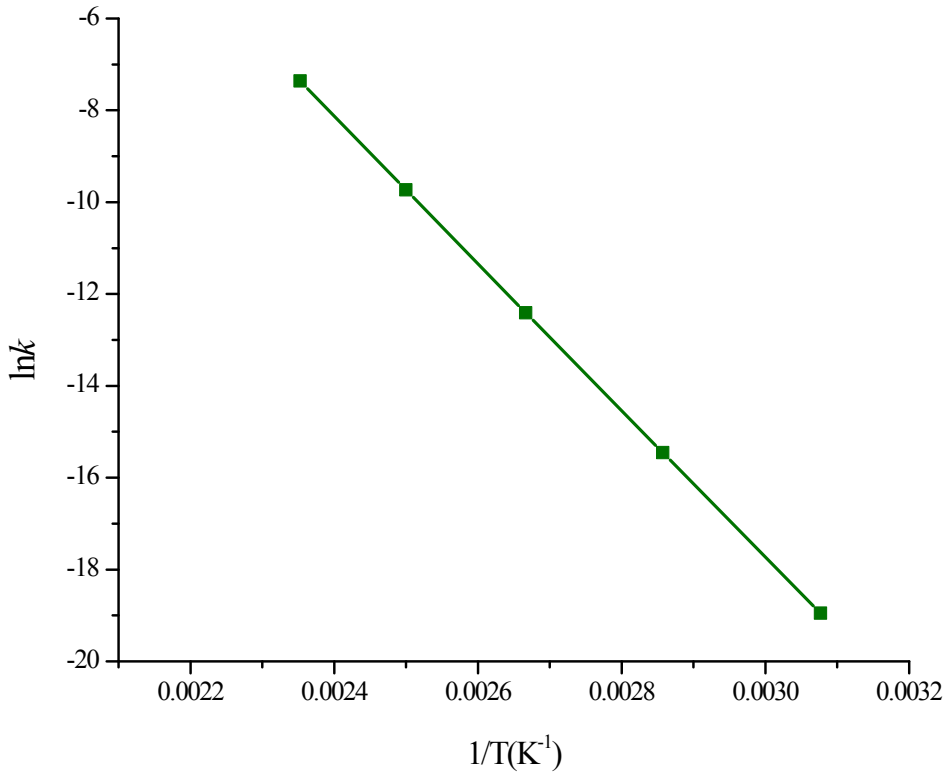


Figure S1: Diagram (relative energies ([V-1]-[V-0]) vs. temperature) showing the stability ranges for the different vanadium doped Al-MCM-41.



0-IM2b 0-TS2b



$$k = 1.43 \times 10^{13} \exp\left(-133074 / RT\right)$$

Figure S2: Arrhenius plots of rate constants for the crucial reaction step of [C-0-bt] 0-IM2b → 0-TS2b in the catalytic oxidation of HMF to DFF catalyzed over [V-0].

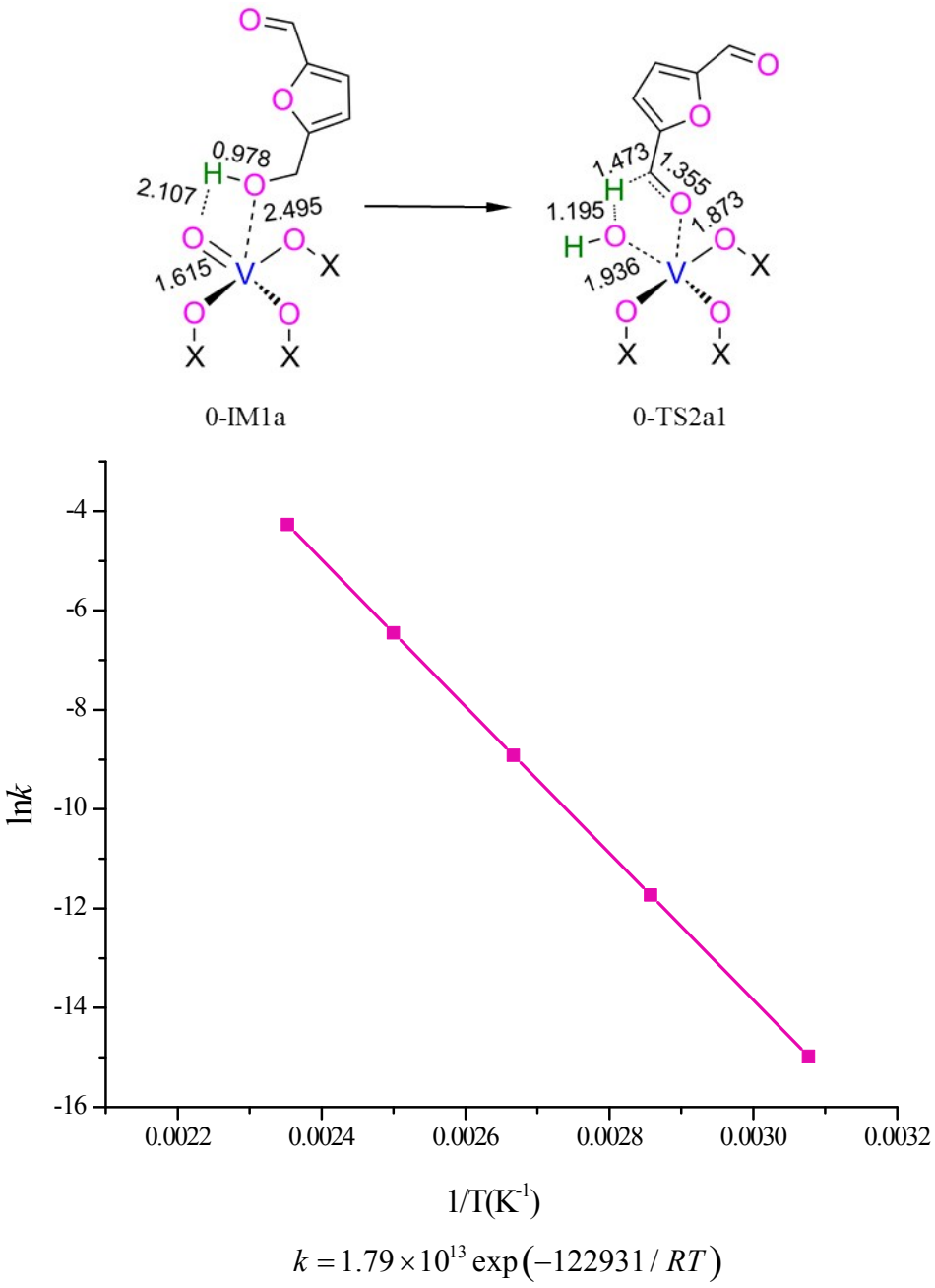
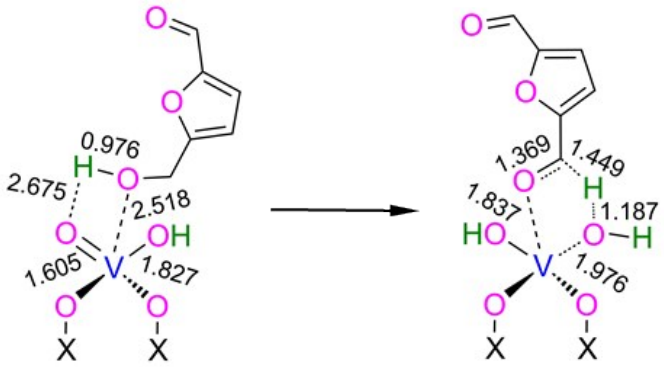
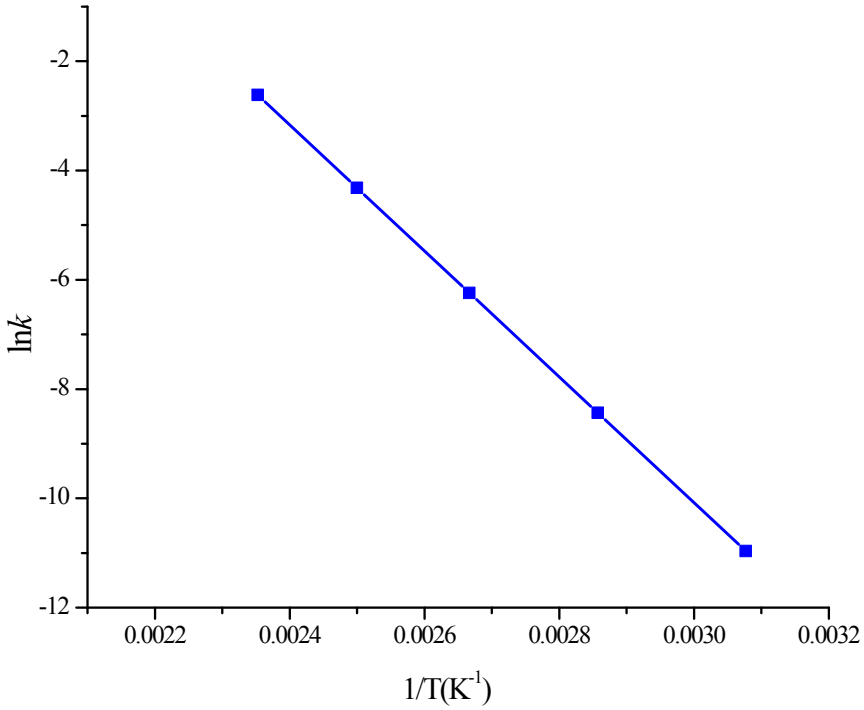


Figure S3: Arrhenius plots of rate constants for the crucial reaction step of [C-0-th] 0-IM1a → 0-TS2a1 in the catalytic oxidation of HMF to DFF catalyzed over [V-0].

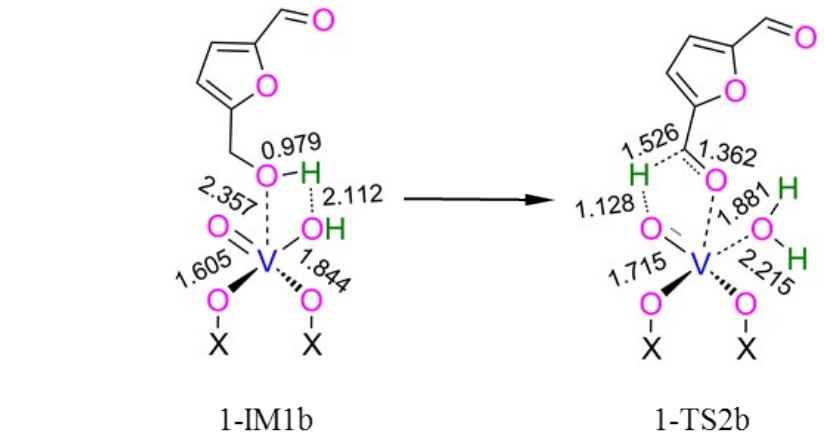


1-IM1a 1-TS2a1

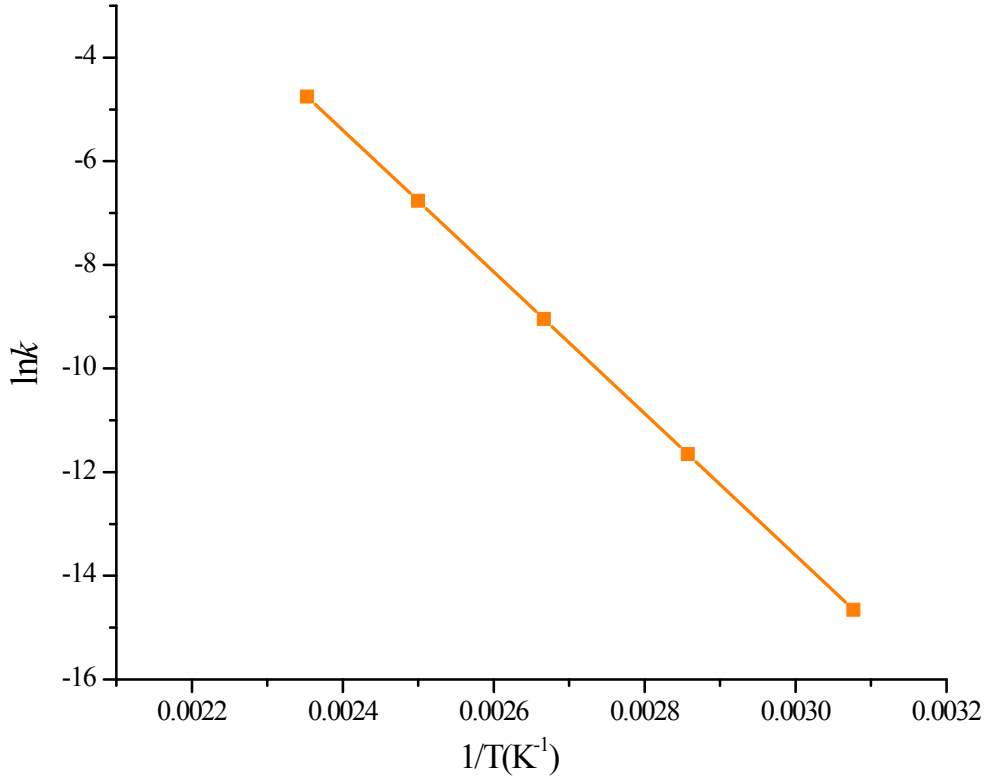


$$k = 4.35 \times 10^{10} \exp\left(-95827 / RT\right)$$

Figure S4: Arrhenius plots of rate constants for the crucial reaction step of [C-1-th] 1-IM1a → 1-TS2a1 in the catalytic oxidation of HMF to DFF catalyzed over [V-1].



1-IM1b 1-TS2b



$$k = 8.24 \times 10^{11} \exp\left(-113744 / RT\right)$$

Figure S5: Arrhenius plots of rate constants for the crucial reaction step of [C-1-ht] 1-IM1b → 1-TS2b in the catalytic oxidation of HMF to DFF catalyzed over [V-1].

Table S1: The pre-exponential factors and activation energy in Equations (i)-(iv) and the TDI and TDTS for the catalytic oxidation of HMF to DFF catalyzed over [V-0] and [V-1].

Active site	Reaction Step (TDI → TDTS)	Rate constant (s^{-1})	Pre-exponential factor	Activation energy (J mol^{-1})
[V-0]	0-IM2b → 0-TS2b	$k_{C\text{-}0\text{-}bt} = 1.43 \times 10^{13} \exp(-133074 / RT)$	1.43×10^{13}	133074
	0-IM1a → 0-TS2a1	$k_{C\text{-}0\text{-}th} = 1.79 \times 10^{13} \exp(-122931 / RT)$	1.79×10^{13}	122931
[V-1]	1-IM1a → 1-TS2a1	$k_{C\text{-}1\text{-}th} = 4.35 \times 10^{10} \exp(-95827 / RT)$	4.35×10^{10}	95827
	1-IM1b → 1-TS2b	$k_{C\text{-}1\text{-}ht} = 8.24 \times 10^{11} \exp(-113744 / RT)$	8.24×10^{11}	113744

Table S2: Sum of electronic energies (E, hartree) and the relative energies (E_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of 2HMF + O_2 → 2DFF + 2H_2O catalyzed over [V-0] at the hybrid quantum mechanics (QM, GGA-PBE/DNP) and molecular mechanics (MM, Universal) calculations.

Species	E	E_r
HMF	-457.54281	
DFF	-456.34675	
$^3O_2$	-150.24664	
O_2	-150.20482	
H_2O	-76.37872	
[V-0]	-3895.55037	
[V-0] + HMF	-4353.09317	0.0
0-IM1a	-4353.10019	-18.4
0-IM1b	-4353.09883	-14.9
0-TS1a	-4353.06566	72.2
0-TS1b	-4353.07739	41.4
0-IM2a	-4353.08208	29.1
0-IM2b	-4353.10407	-28.6
0-TS2a1	-4353.04579	124.4
0-TS2a2	-4353.04180	134.9
0-TS2b	-4353.05136	109.8
0-IM3a1	-4353.06001	87.1
0-IM3a2	-4353.04776	119.2
0-IM3b	-4353.05861	90.8
0-IM4a	-4276.68146	
0-IM4a + H_2O	-4353.06018	86.6
[V-0+2H]	-3896.70006	
[V-0+2H] + DFF	-4353.04681	121.7
0-IM4b	-4503.35455	
0-IM4b – $^3O_2$	-4353.10791	-38.7
^{3}0-IM4b	-4503.33866	
^{3}0-IM4b – $^3O_2$	-4353.09202	3.0
0-IM5a1	-4426.98644	
0-IM5a1 + H_2O – $^3O_2$	-4353.11852	-66.5
^{3}0-IM5a1	-4426.96391	
^{3}0-IM5a1 + H_2O – $^3O_2$	-4353.09599	-7.4
0-IM5a2	-4047.02703	
0-IM5a2 + DFF – $^3O_2$	-4353.12714	-89.2
^{3}0-IM5a2	-4046.99765	
^{3}0-IM5a2 + DFF – $^3O_2$	-4353.09776	-12.0
0-IM5b	-4047.02146	
0-IM5b + DFF – $^3O_2$	-4353.12157	-74.6
^{3}0-IM5b	-4046.98699	
^{3}0-IM5b + DFF – $^3O_2$	-4353.08710	16.0
0-TS3b	-4047.00370	

(Continued Table S1)

Species	E	E_r
0-TS3b + DFF – $^3O_2$	-4353.10381	-27.9
0-IM6b	-4047.00594	
0-IM6b + DFF – $^3O_2$	-4353.10605	-33.8
0-IM7	-4047.01523	
0-IM7 + DFF – $^3O_2$	-4353.11534	-58.2
0-TS4	-4046.99481	
0-TS4 + DFF – $^3O_2$	-4353.09492	-4.6
0-IM8	-4047.02641	
0-IM8 + DFF – $^3O_2$	-4353.12652	-87.5
[V-0+O]	-3970.63538	
[V-0+O] + H_2O + DFF – $^3O_2$	-4353.11421	-55.2
^{3}[V-0+O]	-3970.60058	
^{3}[V-0+O] + H_2O + DFF – $^3O_2$	-4353.07941	36.1
0-IM9a	-4428.18822	
0-IM9a + H_2O + DFF – $^3O_2$ – HMF	-4353.12424	-81.6
0-IM9b	-4428.18553	
0-IM9b + H_2O + DFF – $^3O_2$ – HMF	-4353.12155	-74.5
0-TS5a	-4428.16628	
0-TS5a + H_2O + DFF – $^3O_2$ – HMF	-4353.10230	-24.0
0-TS5b	-4428.16752	
0-TS5b + H_2O + DFF – $^3O_2$ – HMF	-4353.10354	-27.2
0-IM10a	-4428.17340	
0-IM10a + H_2O + DFF – $^3O_2$ – HMF	-4353.10942	-42.7
0-IM10b	-4428.17205	
0-IM10b + H_2O + DFF – $^3O_2$ – HMF	-4353.10807	-39.1
0-IM11a	-4428.16994	
0-IM11a + H_2O + DFF – $^3O_2$ – HMF	-4353.10595	-33.6
0-IM11b	-4428.18906	
0-IM11b + H_2O + DFF – $^3O_2$ – HMF	-4353.12508	-83.8
0-TS6a	-4428.12949	
0-TS6a + H_2O + DFF – $^3O_2$ – HMF	-4353.06551	72.6
0-TS6b	-4428.14832	
0-TS6b + H_2O + DFF – $^3O_2$ – HMF	-4353.08434	23.2
0-IM12a	-4428.28663	
0-IM12a + H_2O + DFF – $^3O_2$ – HMF	-4353.22265	-339.9
0-IM12b	-4428.15670	
0-IM12b + H_2O + DFF – $^3O_2$ – HMF	-4353.09272	1.2
0-IM13	-3971.93657	
0-IM13 + H_2O + 2DFF – $^3O_2$ – HMF	-4353.21933	-331.2
0-TS7	-3971.91439	

(Continued Table S1)

Species	E	E_r
0-TS7 + H_2O + 2DFF – $^3O_2$ – HMF	-4353.19715	-273.0
0-IM14	-3971.93779	
0-IM14 + H_2O + 2DFF – $^3O_2$ – HMF	-4353.22055	-334.4
[V-0] + 2H_2O + 2DFF – $^3O_2$ – HMF	-4353.21185	-311.6

Table S3: Sum of electronic energies (E, hartree) and the relative energies (E_r , kJ mol^{-1}) of various species with respect to the reactants for the reaction of 2HMF + O_2 → 2DFF + 2H_2O catalyzed over [V-1] at the hybrid quantum mechanics (QM, GGA-PBE/DNP) and molecular mechanics (MM, Universal) calculations.

Species	E	E_r
[V-1]	-3165.01545	
[V-1] + HMF	-3622.55826	0.0
1-IM1a	-3622.56329	-13.2
1-IM1b	-3622.56683	-22.5
1-TS1a	-3622.52707	81.9
1-TS1b	-3622.55727	2.6
1-IM2a	-3622.54859	25.4
1-IM2b	-3622.56314	-12.8
1-TS2a1	-3622.51959	101.5
1-TS2a2	-3622.53035	73.3
1-TS2b	-3622.51645	109.8
1-IM3a1	-3622.52934	75.9
1-IM3a2	-3622.56519	-18.2
1-IM4a	-3546.18702	
1-IM4a + H_2O	-3622.56573	-19.6
1-TS3a	-3546.13335	
1-TS3a + H_2O	-3622.51206	121.3
1-IM5	-3546.14676	
1-IM5 + H_2O	-3622.52548	86.1
[V-1+2H]	-3166.16465	
[V-1+2H] + DFF	-3622.51140	123.0
1-IM6	-3696.45067	
1-IM6 + H_2O – $^3O_2$	-3622.58275	-64.3
^{3}1-IM6	-3696.42183	
^{3}1-IM6 + H_2O – $^3O_2$	-3622.55390	11.4
[V-1+2OH]	-3316.49253	
[V-1+2OH] + DFF – $^3O_2$	-3622.59264	-90.3
^{3}[V-1+2OH]	-3316.46624	
^{3}[V-1+2OH] + DFF – $^3O_2$	-3622.56635	-21.3
1-IM7	-3240.10608	
1-IM7 + DFF + H_2O – $^3O_2$	-3622.58491	-70.0
^{3}1-IM7	-3240.06720	
^{3}1-IM7 + DFF + H_2O – $^3O_2$	-3622.54602	32.1
1-TS4	-3240.07898	
1-TS4 + DFF + H_2O – $^3O_2$	-3622.55780	1.2
[V-1+O]	-3240.10726	
[V-1+O] + DFF + H_2O – $^3O_2$	-3622.58609	-73.1
1-IM8	-3697.65363	

1-IM8 + DFF + H_2O – $^3O_2$ – HMF	-3622.58965	-82.4

(Continued Table S2)

Species	E	E_r
1-TS5	-3697.62463	
1-TS5 + DFF + H_2O – $^3O_2$ – HMF	-3622.56065	-6.3
1-IM9	-3697.64126	
1-IM9 + DFF + H_2O – $^3O_2$ – HMF	-3622.57728	-49.9
1-TS6	-3697.60493	
1-TS6 + DFF + H_2O – $^3O_2$ – HMF	-3622.54095	45.5
1-IM10	-3697.75423	
1-IM10 + DFF + H_2O – $^3O_2$ – HMF	-3622.69025	-346.5
[V-1] + 2DFF + 2H_2O – $^3O_2$ – HMF	-3622.67693	-311.6